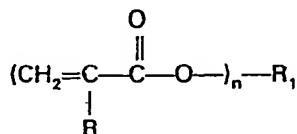


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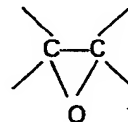
(54) UV and thermally curable, thermoplastic-containing compositions

(57) A UV and thermally curable composition comprises
 (1) (a) a liquid, ethylenically unsaturated monomer, oligomer or prepolymer of the formula:



wherein R is H or CH₃, R₁ is an organic moiety and n is at least 2,

(b) an epoxy resin containing at least 2



groups, or

- (c) a mixture of (a) and (b);
 (2) a thermal initiator,
 (3) a photoinitiator, and
 (4) a thermoplastic material.

Exposure of the composition to UV radiation and heat in seriatim results in a cured solid product which can be utilized as adhesives, coatings, gaskets, sealants, resists and the like.

SPECIFICATION

UV and thermally curable thermoplastic-containing compositions

This invention is directed to radiation and heat activated compositions. More particularly, this invention relates to radiation and heat activated compositions comprising a thermoplastic polymer in combination with a plasticizer for the thermoplastic polymer, a photoinitiator and a thermal initiator.

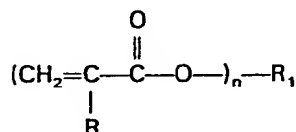
It is known from U.S. Patent 4,020,233 to form cured polythioethers by admixing the composition comprising an ethylenically unsaturated compound containing at least two unsaturated carbon-to-carbon bonds per molecule, a polythiol containing at least two thiol groups per molecule, a photoinitiator and a catalytic amount of a pinacol and, thereafter, subjecting the admixture to UV radiation and heat. It is also known from U.S. 3,652,733 to form cured polythioether products from a composition comprising a polymerizable plasticizer having an average of 2—5 carbon-to-carbon unsaturated groups per molecule, a thermoplastic polymer selected from the group consisting of polyvinyl chloride and copolymers of vinyl chloride with vinyl acetate, a polythiol, and a photoinitiator by exposing said composition to UV radiation after fluxing the thermoplastic polymer at temperatures between 100 and 200°C. The polythiol is a necessary ingredient to assure that the plasticizer is completely cured and thus does not exude from the product. It is further known from U.S. 4,309,331 to form photosensitive dispersions of acrylic resins in combination with a non-volatile ethylenically unsaturated compound and a photoinitiator. It is also known from U.S. 4,288,527 to UV and heat cure in seriatim compositions of unsaturated acrylic or methacrylic monomers or prepolymers in combination with a photoinitiator and a substituted or unsubstituted pinacol. Further, it is known from British Patent Application 2,046,269A to photopolymerize a composition of an epoxidic prepolymer and a vinyl chloride dispersion polymer in the presence of specific photoinitiators which decompose on exposure to electromagnetic radiation.

One object of the instant invention is to produce a composition which can be dual UV and heat cured. Another object of this invention is to produce cured products by exposing the composition to UV radiation followed by the application of heat. Still another object is to produce a composition which, when applied to an irregular surface containing shadow areas inaccessible to UV radiation, will cure in these areas during the heat cure. Yet another object of the invention is to produce a composition which on exposure to UV radiation will skin-cure sufficiently to maintain the composition in situ, e.g., without any runoff or sag so that the composition is properly positioned for the heat cure which follows.

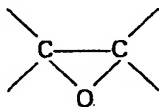
The present invention is directed to a UV and thermally curable composition comprising

(1) a member of the group consisting of

(a) a liquid, ethylenically unsaturated monomer, oligomer or prepolymer of the formula:



wherein R is H or CH₃, R₁ is an organic moiety and n is at least 2,
(b) an epoxy resin containing at least 2



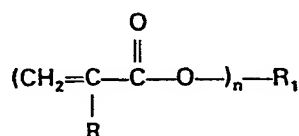
groups, and
(c) a mixture of (a) and (b);
(2) a thermal initiator,
(3) a photoinitiator, and
(4) a thermoplastic material.

In the above composition, the thermoplastic material can be added separately or as a plastisol, e.g., a dispersion of a vinyl resin in a liquid plasticizer. The exposure of the composition to UV radiation and heat in seriatim results in a cured solid product which can be utilized as adhesives, coatings, gaskets, sealants, encapsulants, resists and the like.

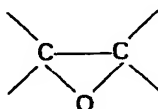
Vinyl chloride homopolymers and copolymers containing same have excellent resistance to chemical attack and to abrasion and have good adhesion properties. They are therefore well suited for use as protective coatings or adhesives. It is sometimes desirable to apply these vinyl resins in the form of a composition containing a plasticizer, e.g., as a plastisol. While it has been proposed to use polymerizable plasticizers, e.g., diallylphthalate, together with a free radical initiator such as t-butyl perbenzoate which reacts on heating, the curing of such plasticizers is difficult to control. Furthermore, in current practice, many heat curable adhesives or sealants are applied at room temperature and then passed through high pressure water cleaning hoses, as in the automotive industry, and then heated to

cause the curing reaction. However, during the passage through the wash-off, some or all of the adhesive or sealant is removed causing gaps in the adhesive or sealant resulting in less adhesion or in inadequate sealing. By use of the composition of the instant invention the composition in the form of an adhesive or sealant can be applied at room temperature, exposed for a short time to UV radiation to set the surface to improve wash-off resistance and eliminate sagging and then can be finally through-cured by heating. Furthermore, in certain systems in which UV light cannot penetrate because of geometrical constraints causing shadow areas or in systems rendered partially UV opaque due to fillers, it is desirable to have a system which is dual UV/heat cured. By use of a dual cure, the composition exposed to the UV light can be radiation cured and the part of the composition in the shadow areas can be heat cured.

It has now been found that cured products can be obtained from a composition comprising (1) a member of the group consisting of (a) a liquid, ethylenically unsaturated monomer, oligomer or prepolymer of the formula:



wherein R is H or CH₃, R₁ is an organic moiety and n is at least 2, (b) an epoxy resin containing at least 2



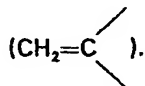
groups, and (c) a mixture of (a) and (b); (2) a thermal initiator, (3) a photoinitiator, and (4) a thermoplastic material

by exposing said composition to UV radiation and then heat in seriatim.

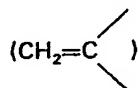
Although the aforesaid compositions, per se, are operable herein to form useful products, they may also be used in combination with conventional copolymerizable monomeric compounds or reactive diluents. The admixture of the composition of the instant invention with other monomers is employed usually to control viscosity and other application variables such as rate of cure as well as final film properties such as hardness and flexibility. Reactive diluents include, but are not limited to, monofunctional acrylic esters, monofunctional methacrylic esters, styrene, vinyl-toluene, acrylonitrile, methacrylonitrile, vinyl chloride, vinylidene chloride, butadiene, isoprene, chloroprene, divinyl benzene, di(vinyl-phenyl) carbonate, diallyl phthalate, diallyl carbonate, di-(allylphenyl) carbonate, diallyl fumarate, triallyl isocyanurate, triallyl cyanurate, diallyl chlorendate, diallyl maleate, butyl glycidyl ether, cresyl glycidyl ether, phenyl glycidyl ether and styrene oxide and unsaturated polyesters and mixtures thereof. By the term unsaturated polyesters herein is meant the usual polycondensation products which consist of ester-like linked residues of polyvalent, especially divalent, alcohols, as well as possibly also residues of monovalent alcohols and/or of monovalent carboxylic acids, selected so that residues must contain at least some unsaturated groups. Examples of acids include maleic acid, fumaric acid, itaconic acid, mesaconic acid, citraconic acid, succinic acid, glutaric acid, adipic acid, phthalic acid, tetrachlorophthalic acid, hexachloroendomethylenetetrahydrophthalic acid, trimellitic acid, benzoic acid, linseed oil fatty acid and ricinoleic fatty acid and mixtures thereof. Examples of alcohols include ethylene glycol, diethylene glycol, propane, butane and hexane diols, trimethylolpropane, pentaerythritol, butanol and tetrahydrofurfuryl alcohol.

The reactive diluents can be added to the system in amounts ranging up to 90% by weight of the ethylenically unsaturated or epoxy compound or combination thereof, preferably 20 to 50% by weight on the same basis.

The thermoplastic material operable herein is any conventional thermoplastic, preferably a vinyl resin. The vinyl resins include both homopolymer and copolymers of vinyl resins from monomers containing the vinyl radical (CH₂=CH—) or vinylidene radical



The term "copolymers" includes terpolymers, tetrapolymers, etc. Vinyl resins from monomers containing the vinyl radical ($\text{CH}_2=\text{CH}-$) or vinylidene radical



operable herein as the thermoplastic material include polyvinyl chloride, polyvinylidene chloride, styrene, polyvinyl acetate, polyvinyl alcohol, polyvinyl formal, polyvinyl fluoride, acrylic and methacrylic acid and their esters. Operable copolymers of vinyl monomers include copolymers of vinyl chloride and vinyl acetate or a copolymer of vinyl acetate with another vinyl monomer. Copolymers of vinyl monomers and alpha-olefin include ethylene-vinyl acetate copolymers, ethylene-acrylic acid, ethylene-ethylacrylate, ethylene-methyl acrylate, vinyl chloride-propylene and ethylene-vinyl alcohol. Recent additions to the PVC group operable herein include graft copolymers in which ethylene-vinyl acetate and ethylene-propylene diene monomer have been incorporated. Mixtures of the above can also be used.

The vinyl resins may be added to the composition per se or in the form of a vinyl plastisol. As used herein, the term "vinyl plastisol" refers to a dispersion of the vinyl resin in a liquid plasticizer.

The liquid plasticizer may be an acrylic or methacrylic monomer, oligomer or prepolymer which not only acts as a plasticizer for the vinyl resin thermoplastic material but also is cured on exposure to UV radiation and heat in the presence of a photo- and thermal initiator. For example, polyvinyl chloride can be admixed with trimethylolpropane triacrylate plasticizer, a photoinitiator and thermal initiator and subjected to UV radiation and heat resulting in a cured homogeneous mass. Epoxidized soya and linseed oils can also be used as reactive plasticizers.

The composition may also contain various conventional non-polymerizable plasticizers for the thermoplastic polymer including, but not limited to, dimethyl adipate, di-n-propyl adipate, diisobutyl adipate, dibutoxyethyl adipate, bis(2-ethylhexyl) adipate, diisodecyl adipate, bis(2-ethylhexyl) azelate, diethylene glycol di-benzoate, dipropylene glycol di-benzoate, octylene glycol di-benzoate, tributyl citrate (acetyl), tris(2-ethylhexyl) citrate (acetyl), triethylene glycol di-2-ethylhexoate, polyethylene glycol di-2-ethylhexoate, butyl phthalyl butyl glycolate, bis(2-ethylhexyl) hexahydroisophthalate, bis(2-ethylhexyl) hexahydrophthalate, hydrogenated terphenyls, bis(2-ethylhexyl) isophthalate, diisodecyl isophthalate, triethyl phosphate, tricresyl phosphate, cresyl diphenyl phosphate, isooctyl diphenyl phosphate, tributyl phosphate, 2-ethylhexyl diphenyl phosphate, isodecyl diphenyl phosphate, tri-n-hexyl phosphate, bis(2-ethylhexyl)phenyl phosphate, tris(2-ethylhexyl) phosphate, diethyl phthalate, dimethyl phthalate, butyl benzyl phthalate, butyl cyclohexyl phthalate, dibutyl phthalate, di-n-hexyl phthalate, butyl octyl phthalate, butyl decyl phthalate, diisooctyl phthalate, bis(2-ethylhexyl) phthalate, di-n-octyl phthalate, dicapryl phthalate, diisodecyl phthalate, di-n-nonyl phthalate, di-n-decyl phthalate, dodecyl phthalate, bis(2-ethylhexyl) sebacate, butyl stearate and bis(2-ethylhexyl) terephthalate. Additionally, polyesters having various tradenames including Plastolein 9720, commercially available from Emery Industries, Inc., Santicizer 462 and 409, commercially available from Monsanto Co., Paraplex G-30, commercially available from Rohm and Haas Co., Harflex 300, commercially available from Harchem Div., Wallace & Tiernan, Inc., NP-10, commercially available from Eastment Chemical Products, Inc., Paraplex G-54, commercially available from Rohm and Haas Co., and Morflex P-50, commercially available from Pfizer & Co., Inc., are also operable herein as nonpolymerizable plasticizers.

The plastisol formulations typically comprise 100 parts of the vinyl resin with 60—100 parts of the plasticizer. The plastisol may include one or more heat stabilizers for the vinyl resin. The amount to be employed is determined by consideration of the temperatures to which the composition must be heated for application and the temperatures which will be encountered in use. Generally about 0.5—5% by weight of heat stabilizer, based on the vinyl resin, will be employed. Conventional heat stabilizers used herein include, but are not limited to, basic lead carbonate, lead acetate, lead stearate, lead oleate, calcium stearate, dibutyl tin dilaurate and barium-cadmium tin complexes.

The relative amounts of the thermoplastic material and the curable group member, i.e., the ethylenically unsaturated compound, epoxy resin or mixture thereof, can vary between wide limits depending on the end use. Thus, weight ratios of the curable group member to the thermoplastic material in the range 20:1 to 1:20, preferably in the range 20:1 to 1:5 are operable herein.

The thermal initiators used herein for curing the ethylenically unsaturated compound of the composition are free radical initiators including, but not limited to, substituted or unsubstituted pinacols, azo compounds, thiurams, organic peroxides, BF_3 adducts and mixtures thereof.

The organic peroxides operable are of the general formula:



wherein $n=0$ or 1, R is independently selected from hydrogen, aryl, alkyl, aryl carbonyl, alkaryl carbonyl, aralkyl carbonyl and alkyl carbonyl and R_1 is alkyl or aryl, said alkyl groups containing 1 to 20 carbon atoms.

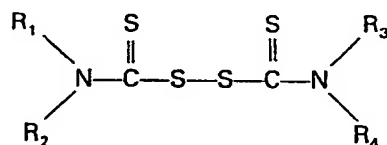
Examples of operable organic peroxides include, but are not limited to 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, 1,3-bis(t-butylperoxyisopropyl)benzene, 1,3-bis(cumylperoxyisopropyl)benzene, 2,4-dichlorobenzoyl peroxide, caprylyl peroxide, lauroyl peroxide, t-butyl peroxyisobutyrate, benzoyl peroxide, p-chlorobenzoyl peroxide, hydroxyheptyl peroxide, di-t-butyl diperphthalate, t-butyl peracetate, t-butyl perbenzoate, dicumyl peroxide, 1,1-di(t-butylperoxy)-3,3,5-trimethylcyclohexane, di-t-butyl peroxide and t-butyl hydroperoxide.

The organic peroxide is added to the composition in an amount ranging from 0.01—10%, preferably 0.1—5%, by weight based on the weight of the ethylenically unsaturated compound.

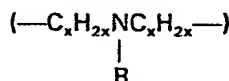
Examples of azo compounds operable herein include, but are not limited to, commercially available compounds such as 2-t-butylazo-2-cyanopropane; 2,2'-azobis-(2,4-dimethyl-4-methoxyvaleronitrile); 2,2'-azobis-(isobutyronitrile); 2,2'-azobis(2,4-dimethylvaleronitrile) and 1,1'-azobis-(cyclohexanecarbonitrile).

The azo compound is added to the composition in an amount ranging from 0.001—5%, preferably 0.01—2% by weight based on the weight of the ethylenically unsaturated compound.

The thiurams operable as thermal initiators herein are of the formula:



wherein R_1 , R_2 , R_3 and R_4 taken singly can be hydrogen, linear or branched alkyl having from 1 to about 12 carbon atoms, linear or branched alkenyl having from 2 to about 12 carbon atoms, cycloalkyl having from 3 to about 10 ring carbon atoms, cycloalkenyl having from 3 to about 10 ring carbon atoms, aryl having from 6 to about 12 ring carbon atoms, aralkyl having from 6 to about 12 ring carbon atoms, and, when taken together, R_1 and R_2 and R_3 and R_4 can each be a divalent alkylene group ($-C_nH_{2n}-$) having from 2 to about 12 carbon atoms, a divalent alkenylene group ($-C_nH_{2n-2}-$) having from 3 to about 10 carbon atoms, a divalent alkadienylene group ($-C_nH_{2n-4}-$) having from 5 to about 10 carbon atoms, a divalent alkatrienylene group ($-C_nH_{2n-6}-$) having from 5 to about 10 carbon atoms, a divalent alkylene oxyalkylene group ($-C_xH_{2x}OC_nH_{2n}-$) having a total of from 4 to about 12 carbon atoms or a divalent alkyleneaminoalkylene group

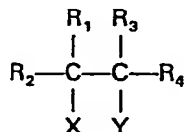


having a total of from 4 to about 12 carbon atoms.

Operable thiurams include, but are not limited to, tetramethylthiuram disulfide, tetraethylthiuram disulfide, di-N-pentamethylenethiuram disulfide, tetrabutylthiuram disulfide, diphenyldimethylthiuram disulfide, diphenyldiethylthiuram disulfide and diethyleneoxythiuram disulfide and the like.

The thiuram is added to the composition in an amount ranging from 0.005—5.0% by weight of the ethylenically unsaturated compound.

The substituted or unsubstituted pinacols operable herein as a thermal initiator have the general formula:



wherein R_1 and R_3 are the same or different substituted or unsubstituted aromatic radicals, R_2 and R_4 are substituted or unsubstituted aliphatic or aromatic radicals and X and Y which may be the same or different are hydroxyl, alkoxy or aryloxy.

Preferred pinacols are those wherein R_1 , R_2 , R_3 and R_4 are aromatic radicals, especially phenyl radical and X and Y are hydroxyl.

Examples of this class of compounds include, but are not limited to, benzopinacol, 4,4'-dichlorobenzopinacol, 4,4'-dibromobenzopinacol, 4,4'-diiodobenzopinacol, 4,4',4'',4'''-tetrachlorobenzopinacol, 2,4-2',4'-tetrachlorobenzopinacol, 4,4'-dimethylbenzopinacol, 3,3'-dimethylbenzopinacol, 2,2'-dimethylbenzopinacol, 3,4-3',4'-tetramethylbenzopinacol, 4,4'-dimethoxybenzopinacol, 4,4',4'',4'''-tetramethoxybenzopinacol, 4,4'-diphenylbenzopinacol, 4,4'-dichloro-4'',4'''-dimethylbenzopinacol, 4,4'-dimethyl-4'',4'''-diphenylbenzopinacol, xanthopinacol, fluorenonepinacol,

acetophenonepinacol, 4,4'-dimethylacetophenone-pinacol, 4,4'-dichloroacetophenonepinacol, 1,1,2-triphenylpropane-1,2-diol, 1,2,3,4-tetraphenylbutane-2,3-diol, 1,2-diphenylcyclobutane-1,2-diol, propiophenone-pinacol, 4,4'-dimethylpropiophenone-pinacol, 2,2'-ethyl-3,3'-dimethoxypropiophenone-pinacol, 1,1,1,4,4,4-hexafluoro-2,3-diphenyl-butane-2,3-diol.

5 As further compounds according to the present invention, there may be mentioned: 5
benzopinacol-mono-methylether, benzopinacol-mono-phenylether, benzopinacol and monoisopropyl ether, benzopinacol monoisobutyl ether, benzopinacol mono(diethoxy methyl)ether and the like.

The pinacol is added to the composition in amounts ranging from 0.01—10%, preferably 0.1—5% by weight based on the weight of the ethylenically unsaturated compound.

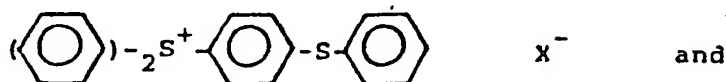
10 The BF_3 adducts used herein as thermal initiators can be used as thermal initiators for both the 10
ethylenically unsaturated compound and the epoxy resin and include, but are not limited to,
 $\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{BF}_3$, $2,6\text{-Et}_2\text{C}_6\text{H}_3\text{NH}_2 \cdot \text{BF}_3$, $\text{EtNH}_2 \cdot \text{BF}_3$, $\text{sec-Bu}_2\text{NH} \cdot \text{BF}_3$, $\text{Et}_2\text{NH} \cdot \text{BF}_3$,

$(\text{C}_6\text{H}_5)_3\text{P} \cdot \text{BF}_3$, $\text{C}_6\text{H}_5\text{NMe}_2 \cdot \text{BF}_3$, Pyridine $\cdot \text{BF}_3$, $\text{Et}_3\text{N} \cdot \text{BF}_3$, $\text{Et}_2\text{O} \cdot \text{BF}_3$ and

15 $(\text{HOCH}_2\text{CH}_2)_3\text{N} \cdot \text{BF}_3$. The BF_3 adduct is added to the composition in an amount ranging from 0.5 to 15
10% by weight of either the ethylenically unsaturated compound, the epoxy resin or the combination thereof, whichever is employed.

To photocure the epoxy resins, it is necessary to use an onium salt. U.S. Patents 4,069,055 and 4,058,401 show radiation induced polymerization of epoxides by the use of certain radiation sensitive onium salts of Group Va, VIa and VIIa elements, in particular various aromatic sulfonium salts. Among

20 the most effective compounds for this purpose are salts of the triarylsulfonium cation containing anions 20
that release Lewis Acid when the salts are photodecomposed. Examples of such salts are:



$(\text{PH})_3\text{S}^+\text{X}^-$ where $\text{X}^- = \text{BF}_4^-, \text{PF}_6^-, \text{AsF}_6^-, \text{SbF}_6^-, \text{SnCl}_6^-, \text{SbCl}_6^-, \text{FeCl}_4^-, \text{BiCl}_5^-, \text{AlF}_6^-, \text{GaCl}_4^-, \text{InF}_4^-, \text{TlF}_6^-, \text{ZrF}_6^-, \text{etc.}$

25 Sulfonium salts of this kind are well known in the literature and have been prepared by a variety 25
of means. (See Pitt, U.S. Patent No. 2,807,648; Knapczyk and McEwen, J. Am. Chem. Soc., 91, 145 (1969); Goethals and Radzitzky, Bull. Soc. Chim. Belg. 73 546 (1964). The complex sulfonium salts can be prepared from the corresponding simple salts, such as the halide salts, by metathesis with a metal or ammonium salt of the complex anion desired as shown in an example hereinafter. These photo-
30 sensitive onium salts are incorporated herein by reference. The onium salts employed as photo- 30
initiators for the epoxy resin are added in an amount ranging from 0.005 to 25% by weight of the epoxy resin.

Thus, when an ethylenically unsaturated group member and an epoxy resin are added in combination to form a thermoset product, in some instances it is necessary to add as a thermal
35 initiator both the aforementioned free radical type and the ionic type in the amounts specified in order 35
to obtain a cured product.

The thermal and photoinitiators can be added to the system in various ways. That is, the initiators, per se, can be admixed with the ethylenically unsaturated or epoxy group member.

40 Additionally, the initiators can be dissolved or suspended in a minor amount of well known 40
commercially available solvents such as ketones, e.g., acetone and methyl ethyl ketone or chlorinated hydrocarbons such as methylene chloride, and then added to the system.

In practicing the instant invention, the components of the composition can be present in widely varying amounts depending on the end use of the composition. That is, the ethylenically unsaturated or epoxy group member or both together can be present in an amount ranging from 5 to 95% by weight
45 with the balance to 100% being made up by the thermoplastic material with or without non-reactive 45
plasticizers, fillers, diluents and other conventional additives. The percentages of thermal and photoinitiators used have previously been set out herein and are based on the weight percent of the ethylenically unsaturated or epoxy group member present.

The compositions of the present invention may, if desired, include such additives as antioxidants,
50 dyes, inhibitors, fillers, pigments, antistatic agents, flame-retardant agents, thickeners, thixotropic 50
agents, surface-active agents, viscosity modifiers, extending oils, tackifiers and the like within the scope of this invention. Such additives are usually preblended with the ethylenically unsaturated compound or epoxy resin prior to or during the compounding step. Operable fillers include natural and synthetic resins, glass fibers, wood flour, clay, silica, alumina, carbonates, oxides, hydroxides, silicates,
55 glass flakes, borates, phosphates, diatomaceous earth, talc, kaolin, barium sulfate, calcium sulfate, 55
antimony oxide and the like. The aforesaid additives may be present in quantities up to 500 parts or more per 100 parts of the ethylenically unsaturated compound, epoxy resin or combination thereof by weight and preferably about 0.005 to about 300 parts on the same basis.

60 Additionally, scavengers and antioxidants such as hydroquinone, pyrogallol, phosphorus acid, 60
tert-butyl hydroquinone, tert-butyl catechol, p-benzoquinone, 2,5-diphenylbenzoquinone, 2,6-di-tert-

butyl-p-cresol, etc., are added to the system in conventional amounts ranging from 0.001 to 2.0% by weight of the ethylenically unsaturated member.

- Epoxy resin stabilizers such as phosphites, e.g., triphenyl phosphite, diphenyl phosphite and trisnonylphenyl phosphite are added to the system in conventional amounts ranging from 0.001 to 2.0% by weight of the epoxy resin.

In practicing the instant invention the composition is preferably subjected to UV radiation followed by heat activation. It is preferable to add photoinitiators in order to initiate the UV reaction. Preferred photoinitiators are the aldehyde and ketone carbonyl compounds having at least one aromatic nucleus attached directly to the



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- group. Various photoinitiators include, but are not limited to, benzophenone, acetophenone, o-methoxy-benzophenone, acenaphthene-quinone, methyl ethyl ketone, valerophenone, hexanophenone, alpha-phenylbutyrophenone, p-morpholinopropionphenone, dibenzosuberone, 4-morpholino-benzophenone, 4'-morpholinodeoxybenzoin, p-diacetylbenzene, 4-aminobenzophenone, 4'-methoxy-acetophenone, benzaldehyde, alpha-tetralone, 9-acetylphenanthrene, 2-acetylphenanthrene, 10-thioxanthene, 3-acetylphenanthrene, 3-acetylundone, 9-fluorenone, 1-indanone, 1,3,5-triacetylbenzene, thioxanthene-9-one, xanthrene-9-one, 7-H-benz[de]anthracene-7-one, 1-naphthaldehyde, 4,4'-bis(dimethylamino) benzophenone, fluorene-9-one, 1'-acetonaphthone, 2'-acetonaphthone, 2,3-butanedione, acetophenone, 2,3-butanedione, benz[a]anthracene 7,12 dione, 2-hydroxy-2-methyl-1-phenylpropan-1-one, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, etc. Another class of photoinitiators is the benzoin ethers, such as benzoin methylether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether, benzoin tetrahydropyranyl ether and 2,2-dimethoxy-2-phenylacetophenone. A third class of photoinitiators is exemplified by diethoxyacetophenone and 2,2-dimethoxy-2-phenylacetophenone. The photoinitiator or mixtures thereof are usually added in an amount ranging from 0.0005 to 30% by weight of the ethylenically unsaturated compound.

- A class of actinic light useful herein for curing is ultraviolet light and other forms of actinic radiation which are normally found in radiation emitted from the sun or from artificial sources such as Type RS Sunlamps, carbon arc lamps, xenon arc lamps, mercury vapor lamps, tungsten halide lamps and the like. Curing periods may be adjusted to be very short and hence commercially economical by proper choice of ultraviolet source, photoinitiator and concentration thereof, temperature and molecular weight and reactive group functionality of the ethylenically unsaturated compound. UV curing periods of about 1 to 5 seconds duration are possible; for example, in coatings, adhesives and encapsulants.

- When UV radiation is used, an intensity of 0.0004 to 60.0 watts/cm² in the 200—400 nanometer region is usually employed.

The heating step requires heating the reactants to at least 80°C, preferably in the range 80°—200°C, for periods ranging from 10 seconds to 30 minutes, in order to form the fully cured product.

- In practicing the instant invention the dual UV/heat curable composition is admixed in any order and applied to the substrate by various conventional means. Following application the composition is exposed to UV radiation for a short period of time, e.g., about 1 second to 1 minute, and, thereafter, exposed to heat by, e.g., passage through a conventional heating oven for a time sufficient to fully cure the composition to a solid product.

- The following examples will aid to explain, but specifically not limit, the instant invention. Unless otherwise noted, all parts and percentages are by weight.

Strength properties of adhesion in shear by tension loading were measured in accord with the procedure set out in ASTM D-1002—72.

Example 1

The following master batches were prepared:

Master batch (1):

	<i>Components</i>	<i>Parts</i>	
	Trimethylolpropane trimethacrylate	4	
	"Paraplex" G-54 ¹	8	
5	PVC-7401 ²	8	5
	"Lupersol" 231 ³	0.2	
	"Darocur" 1173 ⁴	0.2	
	¹ Adipate polyester plasticizer, mol wt 3,000, sp. gravity 1.08, acid number (mg KOH/g) 1.1, saponification (mg KOH/g) 535, commercially available from Rohm & Haas;		
10	² A low fusing vinyl acetate-vinyl chloride copolymer dispersion resin, sp. gravity 1.37, sp. viscosity 1.45 in 1% cyclohexanone at 30°C and K value of 70, commercially available from Diamond Shamrock;		10
	³ 1,1-bis(t-butyl peroxy)-3,3,5-trimethylcyclohexane, commercially available from Pennwalt.		
	⁴ 2-hydroxy-2-methyl-1-phenyl-propan-1-one, commercially available from Merck.		

15 Master batch (2):

	<i>Components</i>	<i>Parts</i>	
	Trimethylolpropane trimethacrylate	4	
	"Paraplex" G-54	8	
	PVC-7401	8	
20	"Lupersol" 231	0.02	20
	"Darocur" 1173	0.02	

Master batch (3):

	<i>Components</i>	<i>Parts</i>	
	Trimethylolpropane trimethacrylate	4	
	"Paraplex" G-54	8	
25	PVC-7401	8	25
	"Darocur" 1173	0.2	
	Benzopinacol	0.2	

Master batch (4):

	<i>Components</i>	<i>Parts</i>	
	Trimethylolpropane trimethacrylate	4	
	"Paraplex" G-54	8	
	PVC-7401	8	
	"Darocur" 1173	0.2	
35	Azobisisobutyronitrile	0.2	35

Master batch (5):

	<i>Components</i>	<i>Parts</i>	
	Trimethylolpropane trimethacrylate	4	
	"Paraplex" G-54	8	
40	PVC-7401	8	40
	"Darocur" 1173	0.2	
	Tetramethylthiuram disulfide ⁵	0.02	

⁵ Recrystallized from boiling chloroform.

Master batch (6):

	<i>Components</i>	<i>Parts</i>	
	Trimethylolpropane trimethacrylate	4	
	"Paraplex" G-54	8	
	"Plivoc" WO-2 ⁶	8	
	"Darocur" 1173	0.2	
50	"Lupersol" 231	0.2	50

⁶ A vinyl chloride dispersion resin, commercially available from Goodyear Chemical.

Master batch (7):

	<i>Components</i>	<i>Parts</i>	
5	Trimethylolpropane trimethacrylate	4	5
	"Paraplex" G-54	8	
	PVC-7401	8	
	"Lupersol" 231	0.2	
	"Irgacure 651"	0.2	

⁷⁾ 2,2-dimethoxy-2-phenyl acetophenone, commercially available from Ciba-Geigy.

Master batch (8):

	<i>Components</i>	<i>Parts</i>	
10	1,6-Hexanediol diacrylate	4	10
	"Paraplex" G-54	8	
	PVC-7401	8	
	"Lupersol" 231	0.2	
	"Darocur" 1173	0.2	

Master batch (9):

	<i>Components</i>	<i>Parts</i>	
20	Trimethylolpropane trimethacrylate	2	20
	Diisononylphthalate	3	
	"Plex"-4858 F ⁸	0.7	
	Benzoyl peroxide	0.1	
	"Darocur" 1173	0.1	

⁸⁾ Terpolymer of 86 parts polymethyl methacrylate, 12 parts polybutyl methacrylate and 2 parts vinyl imidazole, commercially available from Rohm, Darmstadt, West Germany.

Master batch (10):

	<i>Components</i>	<i>Parts</i>	
30	Trimethylolpropane trimethacrylate	3	30
	1,4-butanediol diglycidyl ether	3	
	PVC-7401	4	
	"Darocur" 1173	0.1	
	"Leepoxy" B-550 ⁹	0.1	

⁹⁾ An amine BF₃ adduct, commercially available from Leepoxy Plastics.

Master batch (11):

	<i>Components</i>	<i>Parts</i>	
35	Trimethylolpropane trimethacrylate	4	35
	PVC-7401	8	
	"Lupersol"-231	0.12	
	"Darocur" 1173	0.12	

Master batch (12):

	<i>Components</i>	<i>Parts</i>	
40	1,4-butanediol diglycidyl ether	4	40
	Diphenyl-4-thiophenoxyphenylsulfonium hexafluorophosphate	0.12	
	"Leepoxy" B-550	0.112	
	"Plex"-4858 F	3	

45 The master batches were each made up by combining all the ingredients and stirring until a smooth homogeneous mixture was obtained. The mixture was then deaerated by vacuum. 45

The following examples will show the ability of the above formulations to provide a skin cure to prevent sagging by use of UV radiation alone.

Example 2

Master batch (1) was drawn down on glass substrates to thicknesses of 5, 10 and 30 mils (0.127, 0.254 and 0.762 mm). The coatings were then exposed to UV radiation from an Addalux medium pressure Hg lamp for 1 second. In each instance a skin cure sufficient to hold the coating in place was obtained. The coated substrates were then heated at 140°C in an oven for 25 minutes. A solid, cured coating was obtained in all thicknesses. 5

Example 3

Example 2 was repeated except that master batch (2) from Example 1 was employed and the radiation exposure was 4 seconds. At all thicknesses after heating, a cured, solid coating was obtained.

Example 4

A 1/8" (3.2 mm) thick line of master batch (1) from Example 1 was placed on the overlap of 2 pieces of metal. 2 samples were made up. One of the samples was subjected to UV radiation from an Addalux medium pressure mercury lamp for a 6-second exposure. The 2 samples were then placed under a forceful stream of water to see if any wash-off occurred. The test sample which had not been subjected to UV radiation had a complete wash-off of the line of master batch (1) in less than 1 second. The test samples with the 6-second UV exposure had no wash-off after 6 seconds under the water stream. Wash-off resistance was due to the skin cure covering the line. The UV exposed sample was then heated at 120°C in an oven for 30 minutes. This resulted in a solid adhesive line holding the metal pieces together for each sample. 10 15

Example 5

A 1.5" x 2.125" (3.8 x 5.4 cm) circuit board containing electronic components was completely coated on all sides with an 80 mil (2.03 mm) thick encapsulating coating of master batch (1) from Example 1 by dipping. The thus coated circuit board was exposed for 6 seconds to UV radiation on all sides from an Addalux medium pressure Hg lamp to obtain a tack-free, thick skin cure. The board was then heated in an oven at 120°C at 30 minutes. The coating was a hard, tack-free solid after heading, and the board and components on the board were completely encapsulated. 20 25

Example 6

Master batches (3), (4), (5) and (6) from Example 1 were each applied to glass substrates in a thickness of 30 mils (0.76 mm). The thus coated substrates were then exposed for 4 seconds to an Addalux medium pressure Hg lamp to give a coating with a skin cure. All the substrates were heated at 140°C in an oven for 20 minutes. All the resultant coatings were tack-free solids after heating. 30

Example 7

Master batch (7) from Example 1 was coated on a glass substrate at a thickness of 30 mils (0.76 mm). The coating was then exposed to UV radiation for 2 seconds from an Addalux medium pressure Hg lamp. The thus irradiated coating had a skin cure. Heating in the skin cured coating in an oven at 140°C for 20 minutes resulted in a completely cured solid. 35

Example 8

Master batch (8) from Example 1 was coated on glass substrates to a thickness of 30 mils (0.76 mm). The coating was then exposed to UV radiation for 2 seconds from an Addalux medium pressure Hg lamp. The thus exposed coating was cured on the surface. The thus irradiated coating was then heated in an oven at 140°C for 20 minutes resulting in a completely cured, tack-free solid. 40

Example 9

Example 5 was repeated except that master batch (2) from Example 1 was used. The coating was a hard, tack-free solid after UV radiation and heating at 120°C for 30 minutes. The components on the board were completely coated after heating. 45

Example 10

Master batch (10) from Example 1 was drawn down on glass substrates at a thickness of 30 mils (0.76 mm). The composition was then exposed at a distance of 24" (61 cm) to UV radiation from an Addalux medium pressure Hg lamp for 2 seconds. The coating had a skin cure sufficient to hold the coating in place. The coated substrates were then heated at 140°C in an oven for 30 minutes. A solid, cured, transparent coating was obtained. 50

Example 11

Master batch (9) from Example 1 was drawn down on glass substrates at a thickness of 30 mils (0.76 mm). The composition was then exposed to UV radiation from an Addalux lamp, 24" (61 cm) away, for 5 seconds, to give a skin cure. The coated substrate was then heated in an oven at 80°C for 30 minutes resulting in a tack-free, solid coating. 55

Example 12

Master batch (11) from Example 1 was drawn down on glass substrates at thicknesses of 10 and 30 mils (0.25 and 0.76 mm). The compositions were then exposed at a distance of 24" (61 cm) to UV radiation from an Addalux medium pressure Hg lamp for 2 seconds resulting in a skin cure. The coated substrates were then heated at 140°C in an oven for 20 minutes resulting in solid, tack-free coatings in both thicknesses.

Example 13

Master batch (2) from Example 1 was applied as 1/2" (12.7 mm), 20 mil (0.5 mm) thick lap on as received cold-roll steel and a fiberglass and polyester composite (SMC), commercially available from Budd Co. The thus coated substrates were exposed to UV radiation from an Addalux medium pressure Hg lamp for 3 seconds to form a skin cure. The thus coated substrate was then clamped together with an uncoated substrate of the same material and heated at 140°C in an oven for 20 minutes. The samples were then measured for impact strength and lap shear strength of the adhesive. The adhesive between the steel substrates failed in the adhesive with an impact strength of 12 in.-lb/0.5 in.² (1.36 Nm/3.2 cm²) and an average lap shear strength of 906 psi. (6250 kPa) over an average of 5 samples. The adhesive on the SMC substrate failed in the substrate with an average impact strength of 29 in.-lb/0.5 in.² (3.28 Nm/3.2 cm²) and an average lap shear strength of 848 psi. (5850 kPa) over an average of 5 samples.

Example 14**20 Preparation of diphenyl-4-thiophenoxyphenylsulfonium hexafluorophosphate**

3.15 g of commercially available potassium hexafluorophosphate was added to 150 ml of water. To another container 10 g of a 50% aqueous solution of diphenyl-4-thiophenoxyphenylsulfonium chloride was added to 40 ml of water. This second solution was poured into the first solution with stirring. The resulting white solid product was collected, washed with water and then ether, followed by vacuum drying at 60°C overnight.

6.1 g of this material was dissolved in a mixture of 1 liter of 95% ethanol and 200 ml acetone by boiling. The liquid was reduced to half its volume by bubbling nitrogen through while heating. The remaining liquid containing crystalline product was refrigerated and, thereafter, the pale, yellow-white crystals were collected and washed with ethanol. On drying 3.7 g of solid diphenyl-4-thiophenoxyphenylsulfonium hexafluorophosphate was obtained.

Example 15

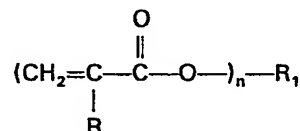
Master batch (12) was drawn down on glass substrates to thicknesses of 5, 10 and 30 mils (0.13, 0.25 and 0.75 mm). The coatings were then exposed to UV radiation from an Addalux medium pressure Hg lamp for 20 seconds. In each instance a skin cure sufficient to hold the coating in place was obtained. The coated substrates were then heated at 140°C in an oven for 25 minutes. An elastic solid, tough, cured coating was obtained in all thicknesses.

Example 16

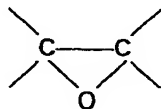
A 1/4" (6.35 mm) thick line of master batch (1) from Example 1 was placed as a sealant on the line of intersection of 2 pieces of metal perpendicular to each other. The sealant line was exposed to UV radiation from an Addalux medium pressure Hg lamp for 3 seconds. A skin cure sufficient to hold the sealant in place and the metal pieces perpendicular to each other resulted. The assembly was then heated at 140°C in an oven for 25 minutes. A solid, cured sealant line resulted.

Claims

1. A UV and thermally curable composition comprising
(1)(a) a liquid, ethylenically unsaturated monomer, oligomer or prepolymer of the formula:



- wherein R is H or CH₃, R₁ is an organic moiety and n is at least 2,
(b) an epoxy resin containing at least 2



- (c) a mixture of (a) and (b);
 (2) a thermal initiator,
 (3) a photoinitiator, and
 (4) a thermoplastic material.
- 5 2. A composition according to claim 1 wherein (1) is (a), (2) is an organic peroxide, (3) is a 5
 benzoin ether and (4) is polyvinyl chloride.
3. A composition according to claim 1 wherein (1) is (b), (2) is a BF_3 adduct, (3) is an onium salt
 and (4) is polyvinyl chloride.
4. A composition according to claim 3 wherein the onium salt is a sulfonium salt.
- 10 5. A composition according to claim 1 wherein (1) is (c), (2) is a BF_3 adduct, (3) is 2-hydroxy-2- 10
 methyl-1-phenylpropane-1-one and (4) is polyvinyl chloride.
6. A composition according to claim 1 wherein (1) is (a), (2) is an organic peroxide, (3) is a
 benzoin ether and (4) is a vinyl acetate-vinyl chloride copolymer.
7. A composition according to claim 1 wherein (1) is (a), (2) is an organic peroxide, (3) is a
 15 benzoin ether and (4) is a methyl methacrylate, butyl methacrylate and vinyl imidazole terpolymer. 15
8. A composition according to any of claims 1 to 7 containing in addition a non-reactive
 plasticizer for the thermoplastic material (4).
9. A composition according to claim 1 substantially as described in any one of the foregoing
 master batches 1 to 12.
- 20 10. A composition according to any of claims 1 to 9 which has been cured. 20
11. A composition according to claim 10 in the form of a sealant, a coating, an encapsulant, or an
 adhesive.
12. A process of forming a cured product which comprises exposing a composition according to
 any of claims 1 to 9 to UV radiation having an intensity in the range 0.004 to 60.0 watts/cm² in the
 25 200—400 nanometer region and, thereafter, heating the composition to a temperature in the range 25
 80—200°C for a time sufficient to obtain a fully cured solid product.
13. A process of forming a cured coating on a substrate which comprises applying to a substrate
 a UV and thermally curable composition according to any of claims 1 to 9, exposing the said
 composition to UV radiation having an intensity in the range 0.0004 to 60.0 watts/cm² in the 200—
 30 400 nanometer region and, thereafter, heating the composition to a temperature in the range 80— 30
 200°C for a time sufficient to obtain a cured solid coating.
14. A process for adhering two substrates which comprises applying to at least one of said
 substrates a composition according to any of claims 1 to 9, exposing said composition to UV radiation
 having an intensity in the range 0.0004 to 60.0 watts/cm² in the 200—400 nanometer region for a
 35 time sufficient to partially cure the composition *in situ*, contacting the substrates with the partially 35
 cured composition therebetween and, thereafter, heating the composition to a temperature in the
 range 80—200°C for a time sufficient to obtain a fully cured solid adhesive.
15. A process for adhering two substrates which comprises contacting said substrates after
 applying to the substrates at a line of contact a composition according to any of claims 1 to 9, exposing
 40 said composition to UV radiation having an intensity in the range 0.0004 to 60.0 watts/cm² in the 40
 200—400 nanometer region to partially cure the adhesive composition and, thereafter, heating the
 composition to a temperature in the range 80—200°C for a time sufficient to obtain a fully cured solid
 adhesive.
16. A process for encapsulating an article which comprises coating said article with a UV and
 45 thermally curable composition according to any of claims 1 to 9, exposing said composition to UV 45
 radiation having an intensity in the range 0.0004 to 60.0 watts/cm² in the 200—400 nanometer
 region to partially cure said coating and hold it in situ, and thereafter, heating the composition to a
 temperature in the range 80—200°C for a time sufficient to obtain a fully cured solid encapsulating
 coating.